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ESTIMATE OF THE SOLUBILITY OF TITANIUM IN BERYLLIUM OXIDE BASED ON QUANTUM-CHEMICAL CALCULATIONS

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The maximum solubility of titanium in BeO is estimated on the basis of calculations of the formation enthalpy of beryllium oxide, doped with titanium, performed using quantum-chemical calculations within the framework of the DFT theory. A method for estimating numerically the maximum solubility of impurities in crystals is examined for beryllium oxide doped with titanium. The method is based on using the results of nonempirical quantum-chemical calculations. The method can be used to estimate the maximum solubility of diverse impurities in inorganic compounds and ceramic materials based on these compounds.

Ceramic based on beryllium oxide BeO possesses unique physical-chemical properties, combining high chemical, thermal, and radiation resistance, thermal conductivity, and a number of other characteristics. This makes it a promising material for use in electronics, new areas of engineering, and special instrument building [1].

It is known [1] that beryllium oxide essentially does not form solid substitution solutions. According to published data [1, 2], the solubility of different elements fluctuates in the range $10^{-3} - 10^{-4}$% (atomic content). On the other hand, impurity defects can have a large effect on the physical-chemical properties and therefore also on the functional characteristics of beryllium oxide (luminescence, exoemission, electric conductivity, and others) [1]. Consequently, it is of interest to develop methods and approaches which make it possible to estimate the maximum solubility of various elements in beryllium oxide.

We have examined the possibility of using the results obtained within the framework of modern quantum-chemical computational schemes based on the electronic density functional theory (DFT) to estimate the maximum solubility of impurities in BeO for the example of the system beryllium oxide – titanium impurity (BeO – Ti).

The formation in beryllium oxide of an impurity defect caused by inclusion of titanium Ti_{Be} was modeled by substituting a titanium atom for a beryllium atom in the initial crystal. In turn, the beryllium atom is removed from the beryllium oxide lattice. This can be represented by the formal reaction

$$BeO + xTi \rightarrow Be_{1-x}Ti_xO + xBe. \qquad (1)$$

For subsequent energy estimates, we performed a quantum-chemical calculation of the electronic structure of the regions indicated above: BeO and $Be_{1-x}Ti_xO$. We used so-called supercells, which model defect-free beryllium oxide and BeO with a point defect Ti_{Be} ($Be_{1-x}Ti_xO$). Their energy spectrum was calculated *ab initio* by the VASP-PAW method [3] with a nonlocal generalized gradient approximation of the exchange-correlation potential (GGA) in the PBE form [4]. The method of tetrahedra was used to integrate over the Brillouin zone [5]. The energy of the plane waves was 400 eV, which gave good convergence. The relaxation effects which appear when an impurity atom is embedded were taken into account by calculating the forces F acting on the atoms. The convergence criterion when optimizing the geometric parameters of a cell corresponded to the condition $F < 0.005$ eV/Å.

To determine the optimal size of the supercells, calculations were performed for a series of BeO cells with wurtzite structure (B4, spac group $C6mc$), containing 16, 32, 72, and 128 atoms. The structure B4 – BeO was given by three parameters: the lattice constants a and c and an internal parameter u which determines the relative displacement of the sublattices of the O and Be atoms along the c axis. The total energy E_{tot} of these supercells as a function of the number of atoms is displayed in Fig. 1. It was found that E_{tot} changes very little as the number of atoms increases above 72. Conse-

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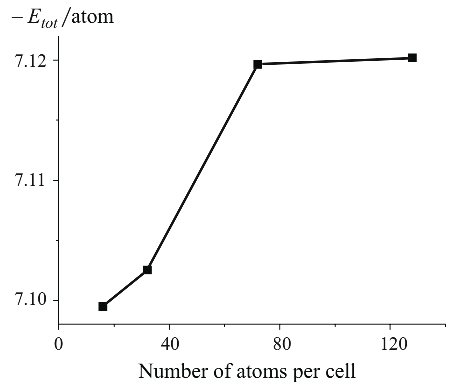

Fig. 1. Total energy E_{tot} of a super cell of wurzite-like beryllium oxide versus the number of atoms.

quently, 72-atom BeO – $Be_{36}O_{36}$ supercells were used in subsequent calculations. The solid solution $Be_{1-x}Ti_xO$, simulated by replacing a beryllium atom with a titanium atom, for such a cell ($Be_{35}Ti_{36}$) corresponded to the formal stoichiometry $Be_{0.972}Ti_{0.028}O$.

As a result, the values of the total energies of $Be_{0.972}Ti_{0.028}O$ and BeO were obtained and found to be – 511.639720 and – 512.615290 eV, respectively.

The formation enthalpy h_{def} of a point defect Ti_{Be} in the system BeO – Ti was estimated as

$$h_{def} = E_{tot}(Be_{35}TiO_{36}) - E_{tot}(BeO)_{36} + \Delta H(Be) - \Delta H(Ti),$$

where $E_{tot}(Be_{35}TiO_{36})$ and $E_{tot}(BeO)_{36}$ are the total energies of the supercells simulating $Be_{0.972}Ti_{0.028}O$ and BeO, respectively; ΔH(Be) and ΔH(Ti) are the heats of formation of beryllium and titanium at the calcination temperatures of the ceramic.

These quantities were taken from the reference literature [5]. Then $h_{def} \approx 84$ kJ/mole for $T \approx 1500$ K.

The Gibbs formation energy of a single defect g_{def} can be determined from the relation

$$g_{def} = h_{def} - T\Delta S_{def},$$

where ΔS_{def} is the entropy change due to the formation of a defect.

In turn, the quantity ΔS_{def} can be estimated from the equation

$$\Delta S_{def} = \Delta S_1 + \Delta S_2 = 3R\ln\frac{1-e^{-\frac{h\nu_0}{kT}}}{1-e^{-\frac{h\nu}{kT}}} + [S(Be) - S(Ti)], \quad (2)$$

where R is the universal gas constant, h is Plank's constant, and k is Boltzmann's constant.

The first term ΔS_1 takes account of the entropy change in Einstein's approximation, due to the difference of the frequencies ν_0 and ν, characterizing the vibrational motion in a crystal without and with defects, respectively. According to the data in [2], $\nu_0 \approx 1500$ cm^{-1} and $\nu \approx 1000$ cm^{-1}. The calculations showed that $\Delta S_1 \approx 5$ J/(mole · K).

The second term ΔS_2 in equation (2) takes account of the difference of the entropies of the final (Be) and initial (Ti) states according to the reaction (1). This quantity can be estimated from the thermodynamic reference data [5], according to which $\Delta S_2 \approx -35$ J/(mole · K) at $T \approx 1500$ K.

Thus, the estimates made for a point defect Ti_{Be} in the system BeO – Ti lead to the values $\Delta S_{def} \approx -30$ J/(mole · K) and $g_{def} \approx 130$ kJ/mole.

When a number of defects Ti_{Be} form, the change ΔG in the Gibbs energy of the system BeO – Ti will be given by the relation

$$\Delta G = N_{def}g_{def} - T\Delta S_{conf},$$

where N_{def} is the number of defects in the crystal and ΔS_{def} is the change in the configuration entropy of the crystal due to the formation of defects.

The quantity ΔS_{conf} is determined by the relation [6, 7]

$$\Delta S_{conf} = R\ln\frac{N!}{N_{def}!(N-N_{def})!}, \quad (3)$$

where N is the total number of sites in the crystal.

The equilibrium value N_{def}^{eq} is obtained from the condition

$$\frac{d(\Delta G)}{dN_{def}} = 0. \quad (4)$$

The solution of equation (4) obtained using Stirling's formula in the relation (3) has the form

$$c_{at} = \frac{N_{def}^{eq}}{N} = \exp\left(-\frac{g_{def}}{RT}\right),$$

where c_{at} is the equilibrium atomic fraction of impurity defects Ti_{Be} in a BeO crystal.

As a result, for the defects Ti_{Be} at $T \approx 1500$ K, taking account of the estimates presented, $g_{def}c_{at} \approx 3 \cdot 10^{-5}$, which agrees well with published data on the low solubility of impurities in the beryllium oxide lattice [1, 2].

In summary, a method for obtaining a numerical estimate of the maximum solubility of impurities in crystals, which is based on using the results of nonempirical quantum-chemical calculations, was examined for beryllium oxide doped with titanium. The method can be used to estimate the maximum solubility of diverse impurities (for example, d and f elements) and inorganic compounds and ceramic materials based on them.

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